Dipolar corrections to the static magnetic susceptibility of condensed ³He

N. Gov

Department of Materials and Interfaces,
The Weizmann Institute of Science,
P.O.B. 26, Rehovot, Israel 76100

We examine the consequences of a recent model describing correlated zero-point polarization of the electronic cloud in solid ³He. This polarization arises from the highly anisotropic and correlated dynamic mixing of the s and p electronic levels ($\sim 1\%$). The magnetic polarization introduces a small paramagnetic correction, of $1 - 0.1\%$, to the static susceptibility of condensed ³He. This correction could explain recent measurements in liquid ³He.

Recent experiments [1] have called attention to the problem of the diamagnetism of condensed phases (liquid and solids) of ³He. Theoretical calculations [2] have not been able to reproduce the relatively large ($\sim 1\%$) observed paramagnetic deviation from the expected value of the electronic diamagnetic response. In the ground-state of the free ³He atom $|0\rangle$ there is no electronic magnetic moment, as the filled s-shell has the two electrons in a singlet state. The static magnetic susceptibility of an insulating material such as ³He is given by [3]

$$\chi = -\frac{N}{V}\frac{e^2}{4mc^2}\langle 0| \sum_i \left(x_i^2 + y_i^2\right)|0\rangle$$
$$+2\mu_B^2\frac{N}{V}\sum_n \frac{|\langle 0|\left(\mathbf{L_z} + g_0\mathbf{S_z}\right)|n\rangle|^2}{E_n - E_0} \qquad (1)$$

where $g_0 \simeq 2$, $\mu_B = e\hbar/(2mc)$ (m is the electron mass) and the applied magnetic field is taken to be in the z-direction, so that only the perpendicular (x, y) projection of the electronic cloud contributes to the first, diamagnetic, term, and only L_z, S_z operators appear in the second, paramagnetic term.

The dynamic corrections to the susceptibility where recently calculated [2], and found a $\sim 0.1\%$ diamagnetic enhancement, with much smaller paramagnetic terms. This calculation was carried out under the assumption of spherical symmetry of the surrounding atomic potential. In our recent work on low density solid He, we showed that in a highly anisotropic potential the local zero-point atomic motion is correlated with electric dipoles arising from the corrections to the Born-Oppenheimer approximation [4]. This model allows us to resolve long-standing problems regarding the experimental data in bcc ³He and ⁴He [4, 5]. In addition we have predicted the appearance of a new excitations mode, which was recently observed by neutron scattering [6]. Following this experimental evidence supporting our model, it seems worthwhile to explore the consequences for the static magnetic susceptibility of He. We show here that our model gives a paramagnetic correction, which is in rough agreement with the observed value of $\sim 1\%$.

We shall now give briefly the main properties of the ground-state dynamic mixing of the s and p-shells in solid He (see more details in [4]). In the low density (specific volume $V < 21$ cm³/mole) bcc phase of He, the potential an atom feels due to the Van-der Waals interactions with its neighbors, has a double-well structure [5, 7], along directions pointing at the next-nearest neighbors. This is due to the average inter-atomic separation (~ 3.5Å) being larger than the minimum of the potential well (~ 2.7Å). Since the potential well is highly anharmonic only along these particular directions, the atoms will make highly directional, large amplitude zero-point oscillations between these double-wells, with typical energy [5] $E_0 \sim 1 - 10$K. We treat this anharmonicity as decoupled from the higher energy modes, which are well described by the usual harmonic approximation [4, 5].

We next couple the anharmonic atomic motion with the atomic polarizations due to the correction to the Born-Oppenheimer approximation [4]. The $s - p$ level mixing is proportional to $\lambda \propto \sqrt{m/M} \sim 1\%$ (where M is the nuclear mass). Such a mixing results in an electric polarization of the electronic cloud, i.e. a zero-point electric dipole moment: $\mu \sim 2\lambda e\langle x\rangle$. When these dipoles (and the atomic motion) on neighboring atoms are uncorrelated, they give a negligible ($\sim 0.1\%$) correction to the usual Van-der Waals interactions.

If the atomic oscillations, and the corresponding electric dipoles, are phase correlated, the crystal can lower its ground state energy by choosing the correct relative phase for the oscillation of adjacent atoms [5]. For the bcc lattice there is long-range order of these relative phases, and the ground-state of the crystal may be described as a global state of quantum resonance between two degenerate configurations which minimize the instantaneous dipolar interaction energy [5]. In our picture, the zero-point energy is resonantly transferred back and forth between the atomic motion and the electronic energy in a coherent way throughout the lattice, with the resonance frequency E_0.

In the hcp and liquid phases we do not expect there to be long-range order in the dipole field, for the following reasons. In the hcp solid the triangular symmetry frustrates long-range ordering of the dipoles [5]. In the liquid, the direction of the instantaneous dipole on each atom is random, so that local correlations should decay

with distance even faster than in the hcp solid. Additionally, the double-wells at different sites are randomly spread over a range of energies E_0, causing the oscillating dipoles to drift out of synchrony. Still, in both these phases we expect local correlations between the dipoles to exist. In order to describe single-atom properties, such as the static susceptibility χ (Eq.1), we will proceed essentially as for the bcc phase.

The first contribution of the p-level mixing to the susceptibility is in the diamagnetic (first) term of Eq.1. Due to the increase in the spatial extent of the electronic cloud the diamagnetism is enhanced by

$$\chi_{dia} = \chi_0 \left(1 + 2\lambda^2 \frac{\langle p|\, x^2 + y^2\, |p\rangle}{\langle s|\, x^2 + y^2\, |s\rangle} \right) \qquad (2)$$

where χ_0 is the usual filled s-shell diamagnetism. Since the ratio of the mean-square spread of the p and s shells is ~ 7, the correction (2) is $\sim 0.1\%$ (using $\lambda \sim 10^{-2}$, as applicable for the lowest density solid [4] and liquid). A correction of this magnitude was also derived in [2].

We now describe an additional correction to the magnetic susceptibility due to the dynamic and highly anisotropic mixing of the electronic levels. The electric polarization of the electronic cloud, has a magnetic polarization associated with it [4], due to the following argument: The mixed p-state of lowest energy is that with the two electrons in the $S = 1$ state, due to electrostatic repulsion, of magnitude ~ 0.25eV. Additionally the spins of the two electrons will tend to align with the axis of the p-shell, due to magnetic dipolar interaction between them. The electronic spins are oriented with the oscillating p-states of the atom, with effective energy $\langle E_{es} \rangle \sim 1.4 \cdot (1 - F(V))$K, where the factor $1 - F(V)$ takes into account the pressure-induced overlap of the different electronic spin orientations [4]. This overlap reduces the effective energy gap and electronic spin polarization: $\langle \mu_e(V) \rangle \simeq (1 - F(V)) \lambda(V) \mu_B$, where $\lambda(V)$ is the volume dependent mixing coefficient. Since the overlap function $F(V)$ is a very steep function of the specific volume V [4], and is $F(V) \sim 0$ at the lowest density, we will take it to be zero in the following calculation. Note that the zero-point mixing of the p-shell with $S = 1$ has zero static expectation value of the magnetic and electric dipole moment.

The paramagnetic (second) term of Eq.(1) is now non-zero. Let us look at p-states orthogonal to the applied magnetic field, i.e. in the x, y-directions. The mixed p-shell of lowest energy is in the S=1 state [4], with the spins aligned along the axis of the p-state (Fig.1), i.e. $|\psi_0\rangle \sim |s, s; S = 0\rangle + \lambda |s, p; S = 1\rangle$, where s, p stand for the orbital angular momenta of the 2 electrons, and $S = 0, 1$ is the spin angular momentum. This describes a mixing of the p-orbital along the x-axis (for example), with the s-orbital, in a spin state $S_x = \pm 1$. An excited state, with respect to $|\psi_0\rangle$, is given by: $|\psi_{ex}\rangle \sim |s, s; S = 0\rangle + \lambda |s, p; S = 0\rangle$, where the p-orbital is mixed with the s-orbital, in a spin state $S_x = 0$. The S_z operator in the second term of Eq.(1) connects between these two levels for mixing in the xy-plane, so we get a term of the form

$$
\begin{aligned}
\chi_{para} &= 2\mu_B^2 \frac{N}{V} \frac{|\langle \psi_0|\, g_0 \mathbf{S_z}\, |\psi_{ex}\rangle|^2}{E_{S_x=0} - E_{S_x=1}} \\
&= 2\mu_B^2 \lambda^4 (1 - F)^2 \frac{N}{V} \frac{|\langle S_x = 1|\, g_0 \mathbf{S_z}\, |S_x = 0\rangle|^2}{E_{es}} \quad (3)
\end{aligned}
$$

where $E_{es} = E_{S_x=0} - E_{S_x=1} \sim 1.4$K is the effective spin-orbit interaction energy difference between the spin aligned and anti-aligned states [4].

Summing over a uniform distribution of the directions of the local oscillating spins relative to the external magnetic field, the value of this correction turns out to be $\chi_{para} \simeq \chi_0 \cdot 10^5 \lambda^4 \sim 1 - 0.1\%$ (again using $\lambda \sim 10^{-2}$). This is of the order of the paramagnetic correction that was recently measured [1] in liquid ^{3}He.

To summarize, using our postulated dynamic and anisotropic $s - p$ mixing in bcc He, we calculate a paramagnetic correction to the magnetic susceptibility. We argue that since the local atomic neighborhood in the liquid is not very different from the low density bcc solid, this paramagnetic correction should appear also in the cold liquid [8]. The small size of the paramagnetic correction, combined with the experimental uncertainties and uncertainties in determining λ, make this effect hard to calculate or observe with accuracy [1, 9].

Acknowledgments

[1] A.G. Mikhalchuk, K.S. White, H.M. Bozler and C.M. Gould, *J. Low Temp. Phys.* **121** (2000) 309; *J. Low Temp. Phys.* **126** (2002) 187.

[2] L.W. Bruch and F. Weinhold, *J. of Chem. Phys.* **113** (2000) 8667; *J. of Chem. Phys.* **117** (2002) 3243.

[3] N.W. Ashcroft and N.D. Mermin, 'Solid State Physics', Saunders College Publishing, 1976.

[4] N. Gov and E. Polturak, *J. Low Temp. Phys.* **128** (2002) 55.

[5] N. Gov and E. Polturak, *Phys. Rev. B* **60** (1999) 1019; N. Gov, *Phys. Rev. B* **62** (2000) 910.

[6] T. Markovich, E. Polturak, J. Bossy, and E. Farhi, *Phys. Rev. Lett.* **88** (2002) 195301.

[7] H.R. Glyde, 'Excitations in Liquid and Solid Helium', Ox-

ford Series on Neutron Scattering in Condensed Matter, 1994.
[8] Where the temperature is much smaller than the atomic zero-point energy.
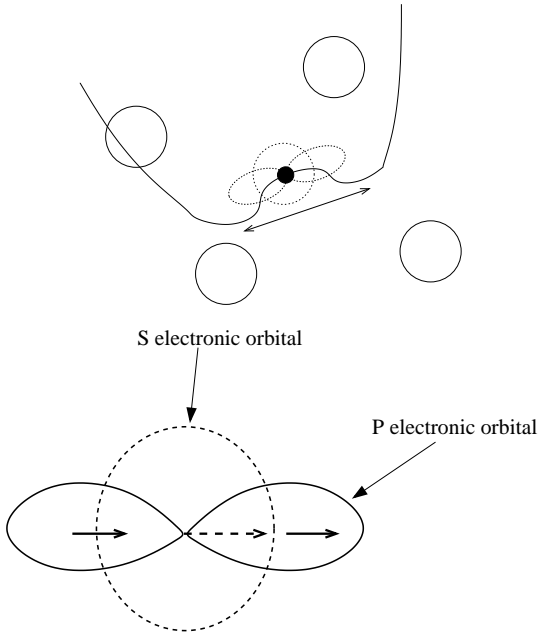[9] H.M. Bozler, private communication.

FIG. 1: The highly directional atomic zero-point motion (solid arrow) in the confining double-well potential of the surrounding atoms (empty circles) in solid or liquid He. This motion of the atom mixes the s and p level along the direction of motion. Lower figure: The spins of the s and excited p electrons align with the axis of the p-state, due to magnetic dipole interaction of strength ~ 1.4K.